NOVEL NON-DESTRUCTIVE MICROWAVE EXTRACTION OF ORGANIC MOLECULES FROM ROCK AND SOIL SAMPLES

Final Report

JPL Task 1022

Luther W. Beegle, Instrument Development and Spectroscopy Research Element (3264)
Isik Kanik, Instrument Development and Spectroscopy Research Element (3264)
Nasser Budraa, Instrument Development and Spectroscopy Research Element (3264)

A. OBJECTIVES

Accurate in situ analysis of astrobiologically important chemical compounds from planetary rocks and soils is strongly dependent on the ability to extract appropriate materials from such samples. In studying the chemical composition of any planetary sample, the most scientifically interesting part of that sample might be inside of it, underneath a protective outer surface. Currently, volatile extraction is limited to the sampling of the surface of a rock or soil via conductive heating or laser ablation. **However, in situ analysis of rock or soil samples for organic molecules would be significantly enhanced by sampling the rock interior, not just its surface.**

Cryptoendolithic microorganisms have been demonstrated to survive in the very hostile dry valleys of Antarctic deserts. They accomplish this by finding protected environments inside rocks, where they grow between the rock crystals (Friedman 1982). Protected by a few cm of a rock from UV radiation and harsh temperatures of their external environment, they flourish in environments that may be analogous to ones which may have existed on the Martian surface. This makes rock interiors a prime spot to look for trace elements and microfossils as evidence of extinct Martian life.

The conventional conductive heating method is perhaps the most straightforward of techniques currently available for use by a landed spacecraft. However, it has three major shortcomings: **inefficient heating, slow response time and high power loss.** Similarly, laser ablation, to extract volatiles from soil/rock samples, is found to be inefficient since heating of the sample is **limited to a small surface area and a very small penetration depth.** Therefore, we propose to use microwave energy to extract compounds of interest (such as organic molecules) from the interiors of soil and rock samples. We present this technique (named the Microwave Enhanced Extraction Technique (MEET)) as a precision tool to selectively remove compounds of interest by volatilization. This process is useful in delivering controlled heating to the interior of a sample, where temperatures can range from just above room temperature (~30º C) to well over 1000º C. This technique simply offers the **best chance** to extract specimens from deep inside Martian soil and rock samples. Because microwave energy is deposited directly into the entire sample without the mediation of conductive heating, the microwave heating process is very efficient without an unnecessary power loss. The sample reaches its vaporization point very rapidly (Barnabas et al. 1995), and the extraction process is very energy-efficient (Lopez-Avila

et al. 1994). For example, it was reported that extraction of pesticides from soil using less than 1 min of microwave radiation was comparable to more than 1.5 hr of traditional heating, and the quality of the extracts was vastly superior (Granzler et al. 1986).

The objective of our proposal was to demonstrate the feasibility of the MEET technique to sublimate trapped atmospheric gases, chemical species and <u>especially</u> organic molecules in soils that could help elucidate questions on Martian abiotic and biotic chemical evolution. Furthermore, we explored the utility of changing the frequency of radiation, attempting to raise the temperature of different species one at a time, and vaporizing them so they could be introduced into a mass spectrometer. Some preliminary experiments on a frequency-tuning approach have already been carried out here at JPL, where pure amino acid samples in a microwave cavity have been shown to sublimate at different frequencies. As shown in **Fig 1.,** ~ 10 mg of proline (115 amu) sublimated within a few seconds at a frequency of 2.393 GHz while ~ 10 mg of alanine (89 amu) sublimated at 2.407 GHz (***<u>both with <8 watts of total power</u>***). By frequency tuning other chemicals present, the host matrix is minimally heated, reducing the amount of heat energy needed.

The proposed proof-of-concept laboratory study will focus on a**)** the utility of selectively extracting molecules of interest by choosing a discrete microwave wavelength that only sublimates certain compounds while ignoring the rest, and b**)** exploring and comparing different MEET procedures (with and without solvent added to the sample of interest). This work will dramatically decrease the power and mechanical complexity of sample introduction into a variety of instruments likely to be included on an in situ astrobiological mission to Mars.

B. PROGRESS AND RESULTS

In this abbreviated work we accomplished the following tasks:

Construction of a new experimental setup. The original apparatus that was going to perform the experiments needed to be redesigned. Amino acids have a freezing point well above room temperature, and this resulted in the sublimated amino acids becoming deposited on the side of the quartz cell. By freezing out, they were not in the gas phase long enough to be analyzed by the mass spectrometer. A new experimental setup in which the mass spectrometer was placed right above the microwave chamber allowed enough amino acids to enter the mass spectrometer to be analyzed. The experimental schematic is shown in Fig 1. In addition, due to laboratory space requirements, the experiment was moved from 183-256 to its new and present home in 183-623. This required putting in a new fume hood which took several months to complete.

Performed experiments on amino acids with discrete wavelengths. We confirmed the preliminary experimental results that amino acids could be sublimated at different microwave frequencies. We placed 100 mg of pure amino acid in the microwave cavity and flooded the cavity with discrete microwave frequencies. Fig 2 shows the difference in excitation frequencies for alanine and proline. Fig 3 shows the mass spectra of alanine at three different frequencies. The peaks at 49 amu and 61 amu are fragments of alanine (89 amu) due to the electron impact source on the mass spectrometer.

Preformed microwave extraction experiments on field samples. We studied a limestone sample, obtained from Wards Scientific, made primarily out of calcite, which is $CaCO_3$. This was confirmed by x-ray diffraction spectroscopy (Beegle et a. 2004). Figure 4 shows the spectra of limestone obtained by our quadrupole mass spectrometer at both 1 and 5 watts. While no peaks were seen at 1 watt, at 5 watts of power, mass peaks are easily seen that correspond to $CaCO_3$ and its fragmentation products. Furthermore, when alanine is added to the material it clearly can be sublimated as is shown in Figure 4. Our spectrometer, a Ferrin mass spectrometer, did not posses the resolution to clearly distinguish peaks, but a comparison of spectra of pure limestone and pure alanine, as well as a chemical analysis of the leftover sample, make it clear that both species were vaporized. What is not clear and needs further exploration is whether the fragmentation of the calcite takes place in the microwave extraction or due to the electron impact source.

C. SIGNIFICANCE OF RESULTS

The work on limestone seems to indicate that it is possible to sublimate mineral phases utilizing microwave radiation. However, when mixtures were introduced into the cavity, it made the mass spectrometer data hard to analyze. The mass spectrometer that we utilized did not have the resolution at mass > 50 amu to differentiate different species. Obtaining a different mass spectrometer for analysis is a must so that different species can be resolved.

One very significant aspect of this DRDF task is that the work that was started here was submitted to the Astrobiology Science and Technology Instrument Development (ASTID) Program, and was awarded $650,000 over the next 3 years to continue this important work.

D. FINANCIAL STATUS

The total funding for this task was $40,000, all of which has been expended.

E. PERSONNEL

No other personnel were involved.

F. PUBLICATIONS

None.

G. REFERENCES

[1] **Beegle L.W.**, A. Tsapin, W. Abby, D. Dragoi, and I. Kanik Organic molecule extraction from terrestrial sedimentary deposits using heat, H_2O and HCl extraction. To be submitted to Astrobiology, January 2004

H. APPENDIX:

NOVEL NON-DESTRUCTIVE MICROWAVE EXTRACTION OF ORGANIC MOLECULES FROM ROCK AND SOIL SAMPLES

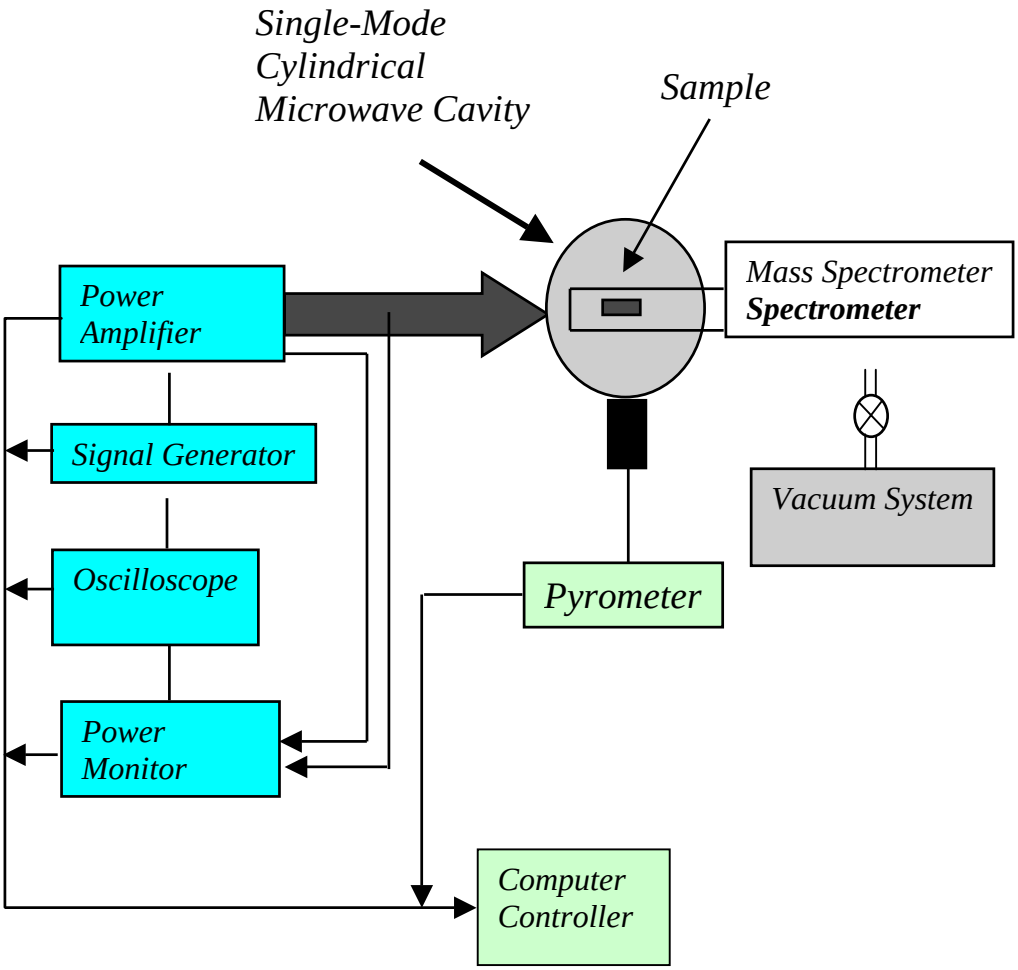

Fig 1. Schematic of the experimental setup. In the new setup, the mass spectrometer is directly outside of the microwave cavity.

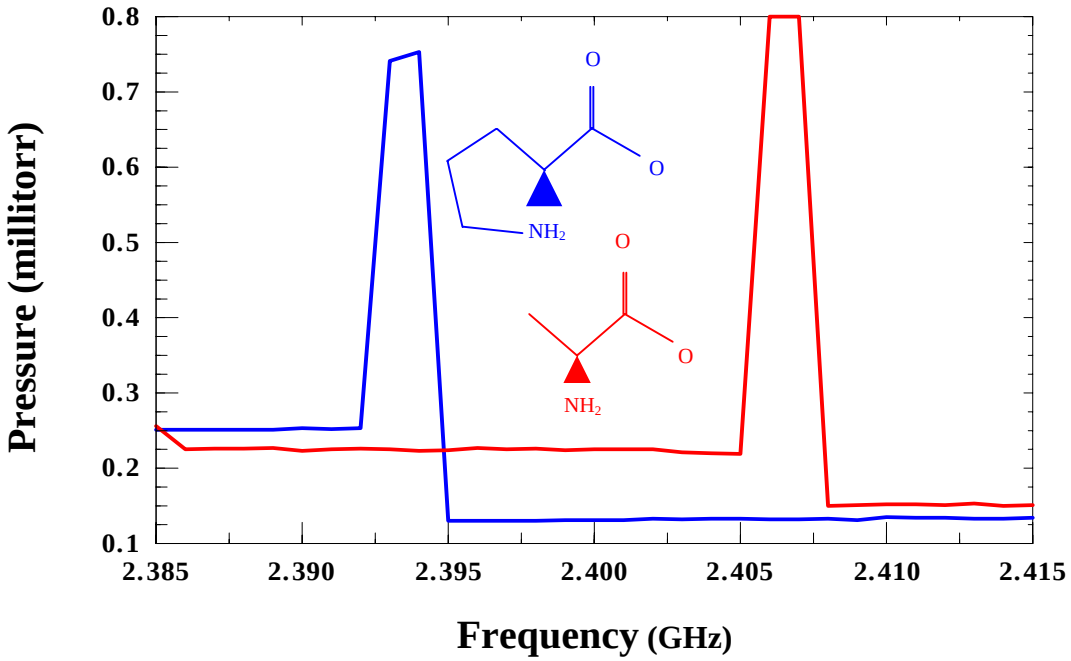

Fig 2. Pressure vs microwave-cavity frequency for two amino acids, Proline (*left*) and Alanine (*right*), in the same microwave cavity along with structural diagrams.

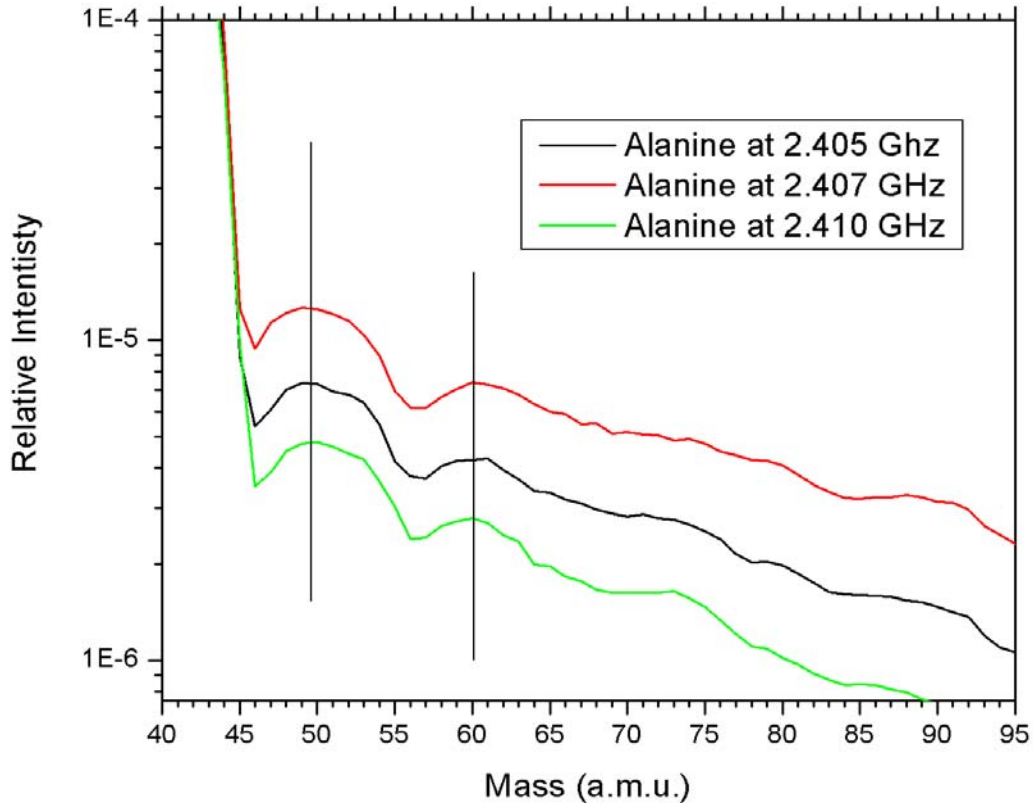

Fig 3 The amino acid alanine was placed in the microwave cavity (see Fig 1.) and excited by various microwave frequencies. At 2.407 GHz, the alanine was most easily sublimated, while at different wavelengths less vaporized. This was a confirmation of our earlier results.

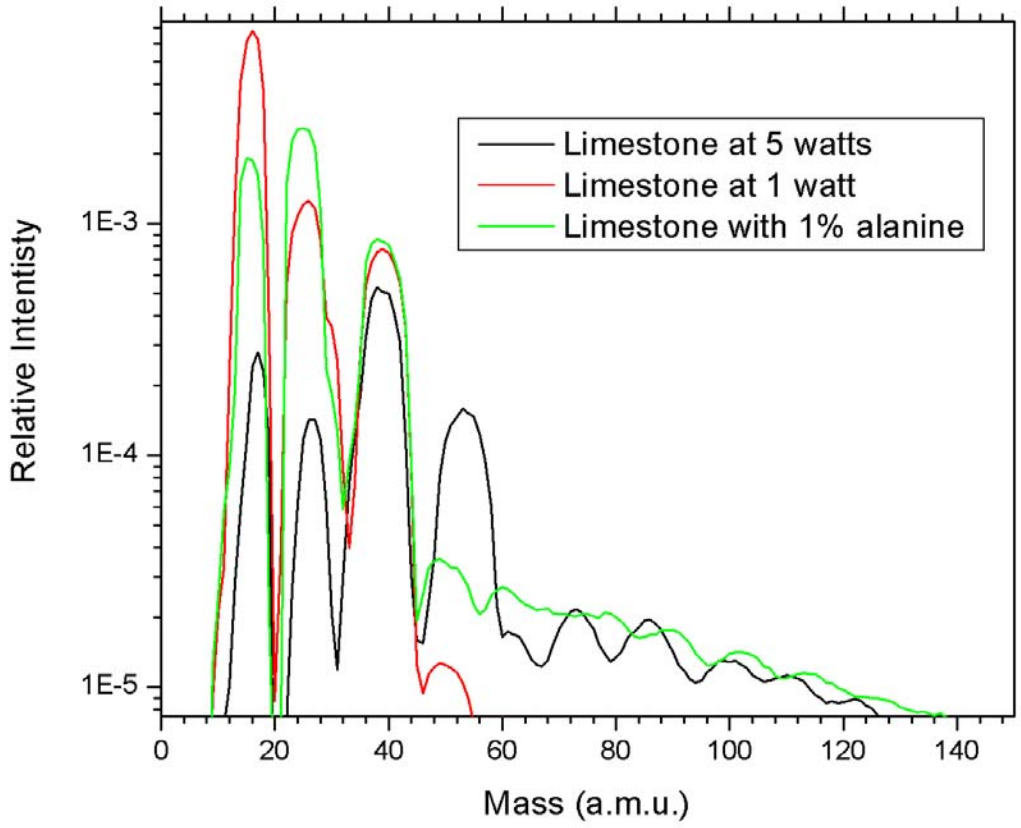

Fig 4. 3 different samples placed in the microwave cavity shown in Fig 1. Pure limestone, $CaCO_3$, and its fragmentation patterns are clearly visible at 5 watts of power, while no signal is detected at 1 watt. When 1% alanine was in the microwave, the mass spectra identified both calcite and alanine which were vaporized and introduced into the mass spectrometer.